

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

DECEMBER 22nd 1999

Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM ANSWER BOOKLET AND COMPUTER ANSWER SHEET.

The examination consists of Parts 1 - 9, each of which should be attempted. Note that some Parts provide you with a choice of questions, *i.e.* answer 4 out of 5. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 6 will be computer graded, and only Parts 7, 8, and 9 are to be answered on the answer pages provided. A periodic table with atomic numbers and atomic weights is appended to the exam.

Parts 1 - 6 consist of a series of multiple choice questions numbered 1 - 45, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and **not ink**. In some cases it is required that you indicate **multiple** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out **both** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased **cleanly**.

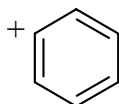
Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**.

PART 1 RELATIVE PROPERTIES**20% ANSWER ANY TEN (10) OF QUESTIONS 1 TO 14.****Arrange the items in questions 1-14 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.**

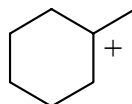
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

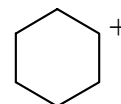
1. The relative stability of the following carbocations:



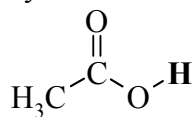
(i)



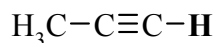
(ii)



(iii)

2. Acidity of the **H** shown in bold:

(i)

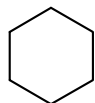


(ii)

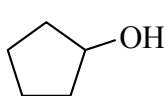


(iii)

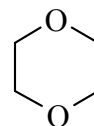
3. The boiling points of the following:



(i)



(ii)



(iii)

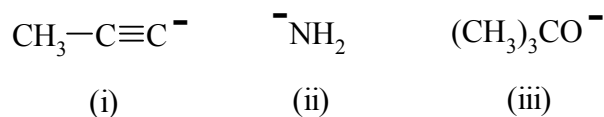
4. The number of types of hydrogen in each of the following:

- (i) 3-methylpentane
- (ii) n-hexane
- (iii) cyclohexane

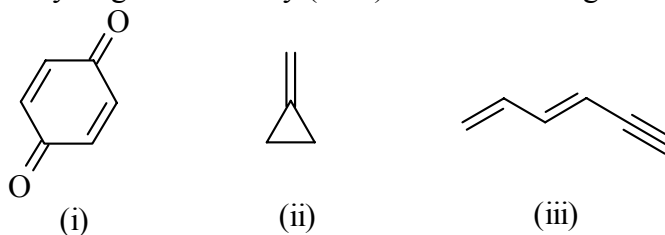
Use the following code to indicate your answers.

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|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

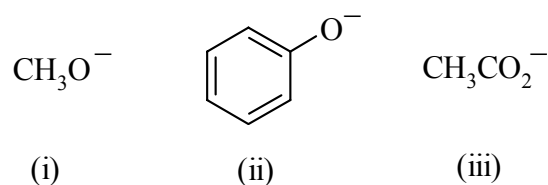
5. The relative basicity of the following:



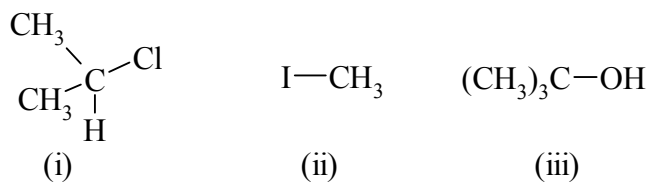
6. The index of hydrogen deficiency (IHD) of the following:



7. The relative nucleophilicity in polar, protic solvents of the following:



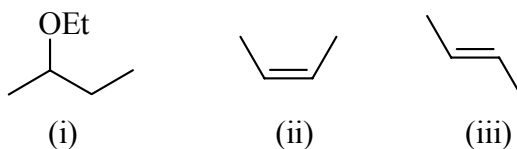
8. Rate of reaction of the following, with NaCN in DMSO:



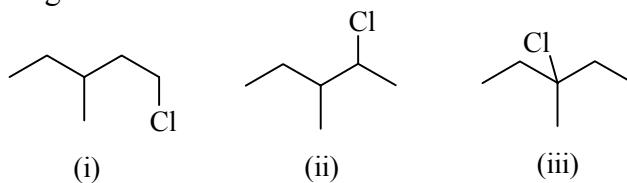
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

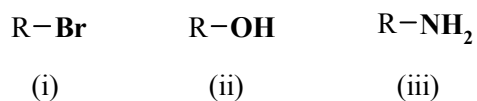
9. The relative yields of the following products from the reaction of 2-bromobutane with sodium ethoxide in ethanol at 55°C:



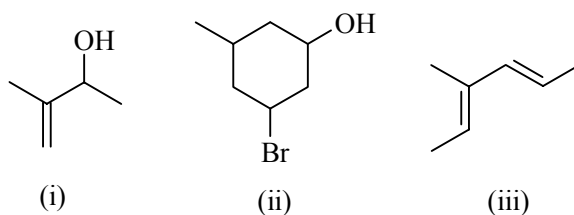
10. The relative yields of the following products from the reaction of 3-methylpentane with Cl₂ / UV light:



11. The leaving group ability of the group shown in **bold** in each of the following:



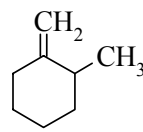
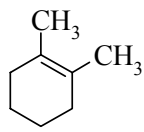
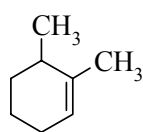
12. Number of stereoisomers of:



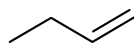
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

13. The relative stability of the following alkenes:



14. The relative rate of reaction of the following alkenes with HCl:



PART 2: LABORATORY

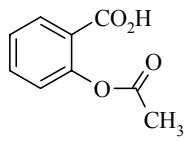
10% ANSWER ALL FIVE (5) OF THE QUESTIONS 15-19.

Questions 15-19 are based on the reactions covered in the laboratory experiments.

In each case select ALL of the statements that are true.

In some questions, MORE THAN ONE STATEMENT MAY BE CORRECT.

15. Identify the correct statement(s) related to the “Chromatography” experiment:
- A Chromatography is based on the partitioning of the solute between a stationary phase and a mobile phase.
 - B The R_f value is defined as (distance solvent front moves)/(distance solute spot moves).
 - C If two spots have the same R_f value, then they must be the same compound
 - D The analgesics were visualised using ninhydrin.
 - E The structure of aspirin is

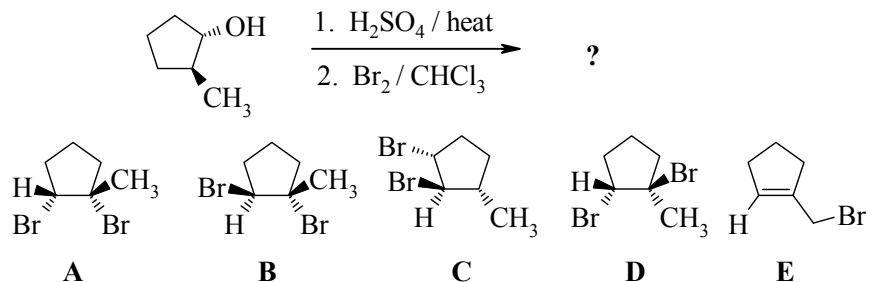


16. Choose the correct statement(s) related to the experiment “Reaction of Alcohols”:
- A The reaction of *t*-butanol with a solution of zinc chloride in HCl (Lucas reagent) is too slow and the rate determining step is the coordination of the zinc chloride to the hydroxyl group.
 - B Zinc chloride is a Lewis base. Its function is to interact with the hydroxyl group of the alcohol.
 - C The Lucas reagent can be used to distinguish between 1°, 2° and 3° alcohols.
 - D The rate-determining step of the reaction of an alcohol with a hydrogen halide (such as HCl or HBr) is the protonation of the hydroxyl group.
 - E Dehydration of a 3° alcohol requires 80-90% of H₂SO₄ and a reaction temperature above 140°C.

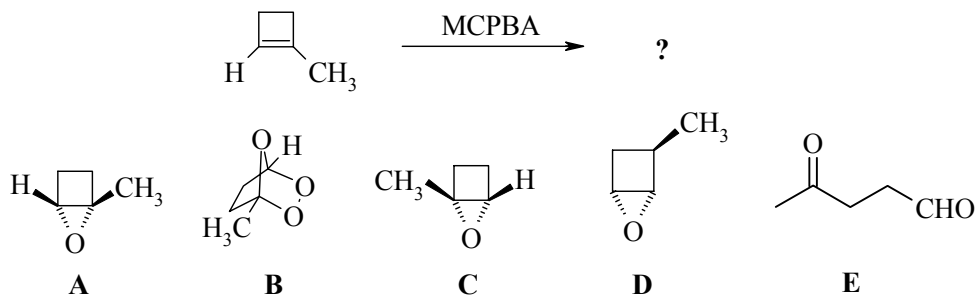
17. In the experiment "Reactions of Alcohols", 2,4-dinitrophenylhydrazine (2,4-DNP) was used to:
- A test for the formation of alkenes from the reaction of an alcohol with chromic acid.
 - B test for the formation of a chromate ester.
 - C form a precipitate with a carboxylic acid from the over oxidation of an aldehyde.
 - D detect the formation of a ketone from a 2° alcohol and/or an aldehyde from a 1° alcohol.
 - E distinguish between 1°, 2° and 3° alcohols, because 2,4-DNP forms an insoluble coloured precipitate with alcohols.
18. In the experiment "Reactivity in Substitution Reactions", which of the statements about the reactions with NaI / acetone are true ?
- A the reaction conditions favour an SN1 reaction.
 - B the iodide ion is a good nucleophile.
 - C the precipitate that forms is the sodium halide salt.
 - D the secondary bromide reacted the fastest under these reaction conditions.
 - E bromine is a better leaving group than chlorine.
19. In the experiment "Reactivity in Substitution Reactions", which of the statements about the reactions with AgNO₃ / aq. ethanol are true ?
- A the polar solvent system favours the formation of the carbocation.
 - B the nitrate ion is a good nucleophile.
 - C the precipitate that forms is the silver halide salt.
 - D the primary bromide reacted the fastest under these reaction conditions.
 - E the nucleophile was either H₂O or EtOH.

PART 3: PRODUCTS OF SYNTHESIS**10% ANSWER ANY FIVE (5) OF QUESTIONS 20-25.****For each of questions 20-25 select the major product(s) obtained using the reaction conditions indicated by selecting from the list of compounds provided.**

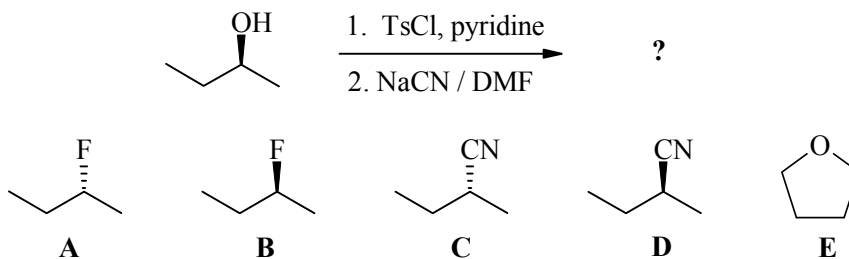
20.



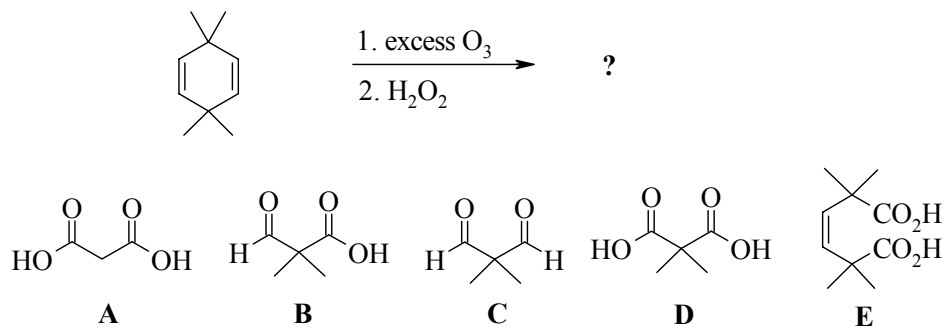
21.



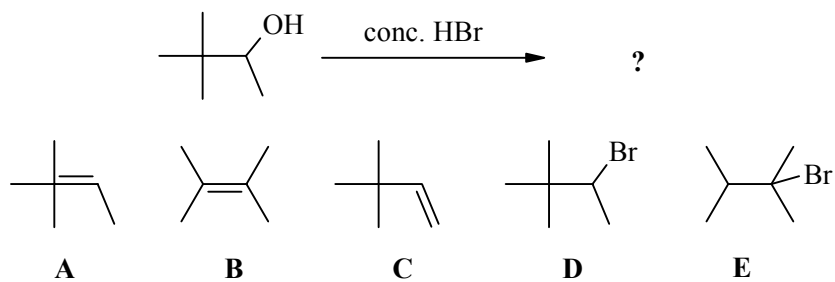
22.



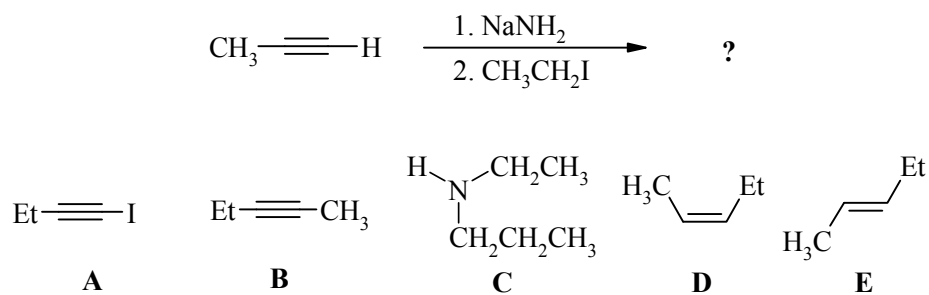
23.



24.

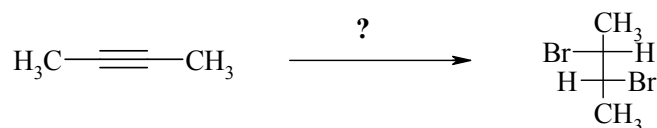


25.



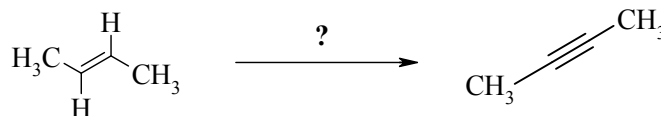
PART 4: REAGENTS FOR REACTIONS**10% ANSWER ANY FIVE (5) OF THE QUESTIONS 26-31.****For each of questions 26-31, select the BEST reagent combination from the list provided to complete the reaction sequence shown:**

26.



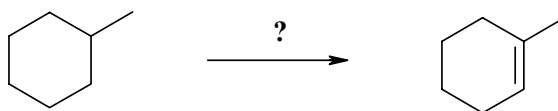
- A i) Na / NH₃ (l) ii) Br₂ / CHCl₃
 B i) Na / NH₃ (l) ii) Br₂, uv light
 C i) H₂ / Pd / CaCO₃ / pyridine ii) Br₂ / CHCl₃
 D i) H₂ / Pd / CaCO₃ / pyridine ii) HBr
 E i) excess H₂ / Pd ii) Br₂, uv light

27.



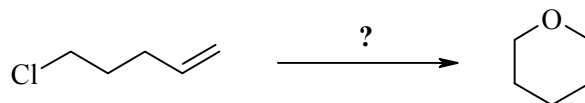
- A i) HBr ii) KOH / heat
 B i) MCPBA ii) NaOH
 C H₂ / Pd / pyridine / CaCO₃
 D i) Br₂ / CHCl₃ ii) NaNH₂
 E KOH / heat

28.



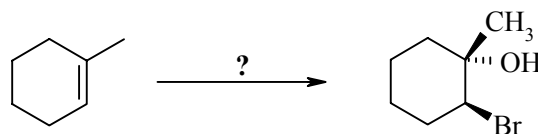
- A H₂ / Pd
 B i) HCl ii) KOH / EtOH / heat
 C i) SOCl₂ / Et₃N ii) KOH / EtOH / heat
 D i) Br₂ / hv ii) KOH / EtOH / heat
 E i) H₂O ii) H₂SO₄ / heat

29.



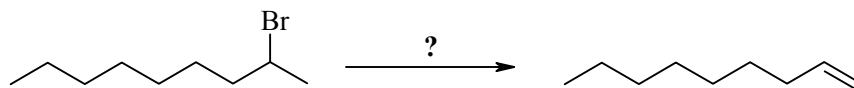
- A i) H_2O ii) NaOH
 B i) aq. H_2SO_4 ii) Na
 C HBr / peroxides
 D i) BH_3 then $\text{NaOH} / \text{H}_2\text{O}_2$ ii) NaI / acetone
 E $\text{NaOH} / \text{H}_2\text{O}$

30.



- A i) $\text{Br}_2 / \text{CHCl}_3$ ii) NaOH
 B i) NaOH ii) NaBr
 C i) BH_3 then $\text{NaOH} / \text{H}_2\text{O}_2$ ii) HBr
 D $\text{Br}_2 / \text{H}_2\text{O}$
 E i) aq. H_2SO_4 ii) tosyl chloride, Et_3N iii) NaBr

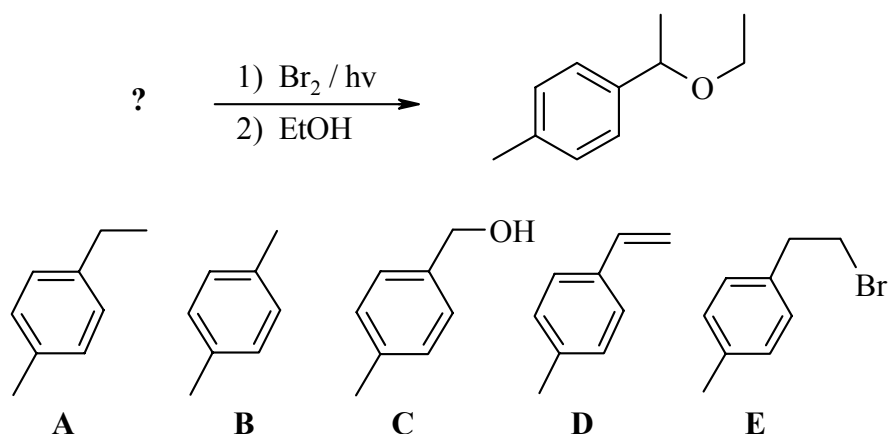
31.



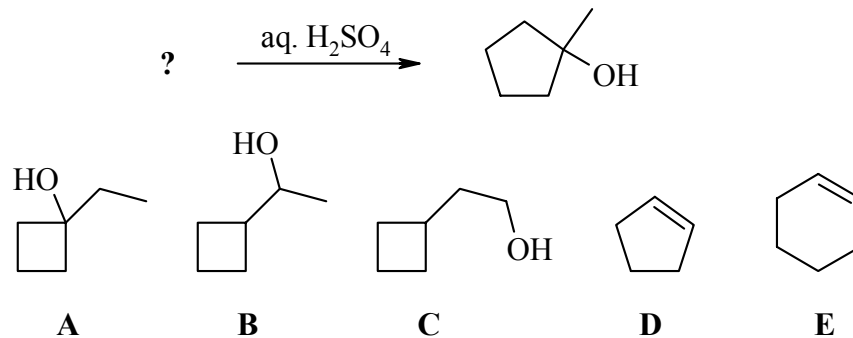
- A conc. H_2SO_4 / heat
 B $\text{KOH} / \text{EtOH} / \text{heat}$
 C $\text{AgNO}_3 / \text{aq. EtOH}$
 D aq. NaOH
 E $\text{KOtBu} / \text{DMSO} / \text{heat}$

PART 5: STARTING MATERIALS**10% ANSWER ANY FIVE (5) OF QUESTIONS 32-37.****For each of questions 32-37, choose from the lists provided the appropriate starting material that would give the product shown under the reaction conditions indicated:**

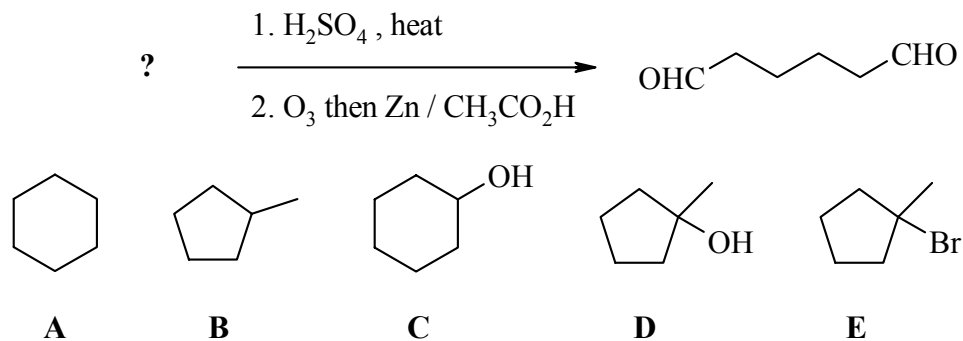
32.



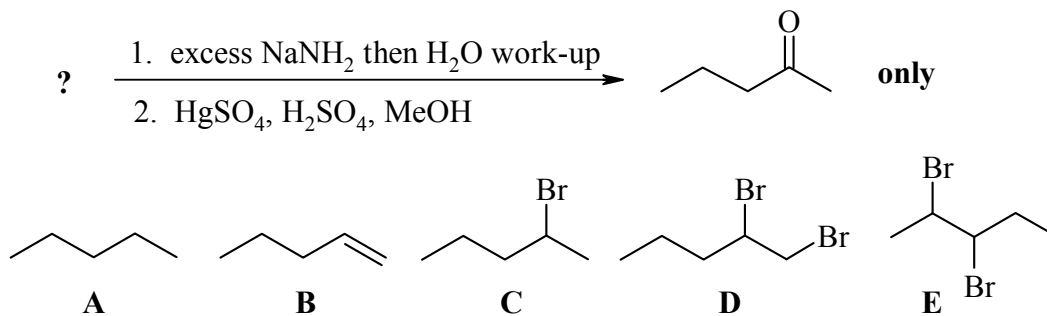
33.



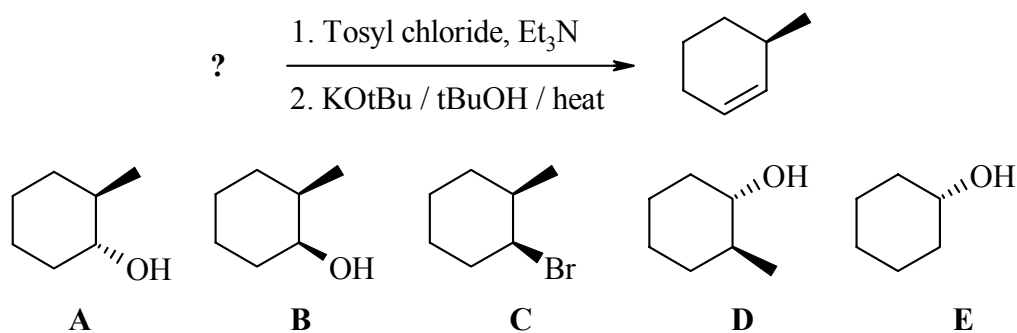
34.



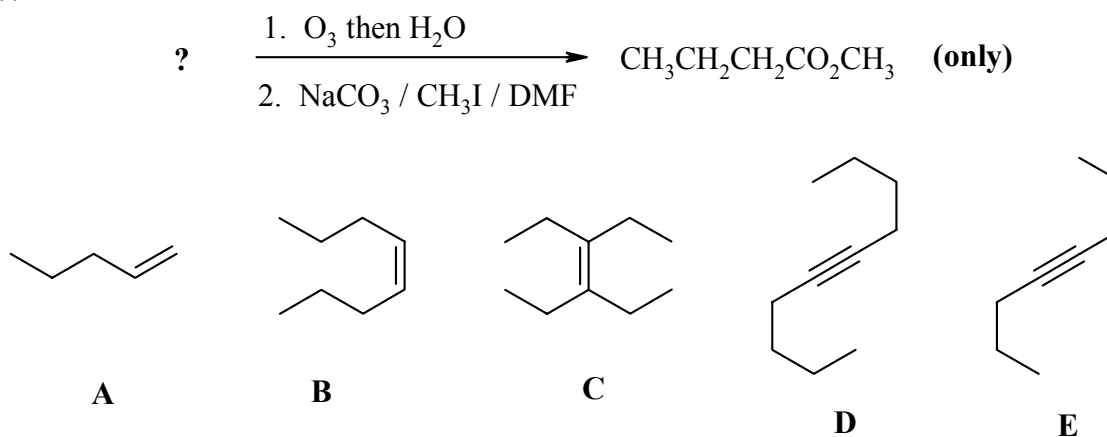
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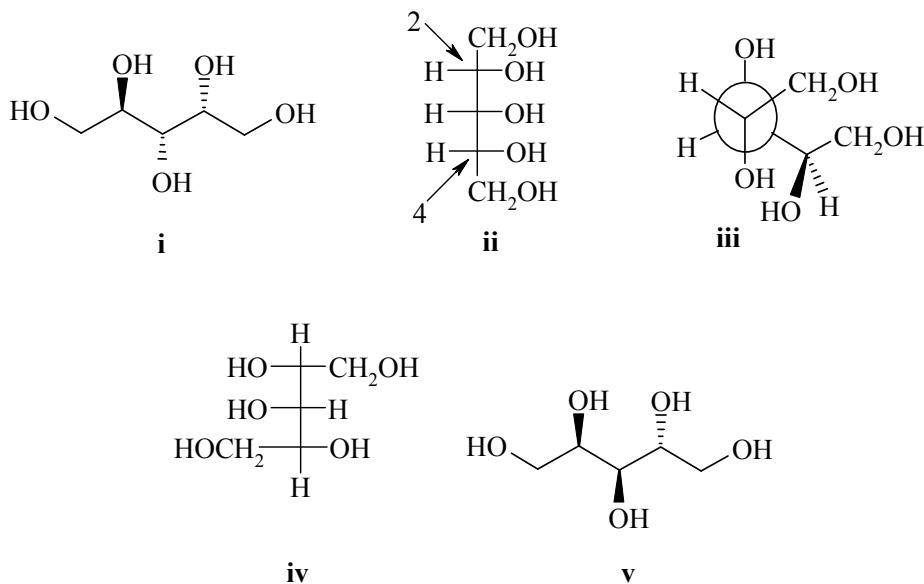


36.



37.



PART 6: STEREOCHEMISTRY**10% ANSWER ALL OF THE QUESTIONS 38-45.****Based on the following five structures (i-v) shown below, answer questions 38-45.**

38. What type of isomers are **i** and **iv** ?
(1 mark)
- A identical B enantiomers C diastereomers D conformational E constitutional
39. What type of isomers are **i** and **iii** ?
(1 mark)
- A identical B enantiomers C diastereomers D conformational E constitutional
40. If the specific rotation of **i** is -60.0° , what is the specific rotation of **iii**, if 1.0 g of **iii** is dissolved in 10 mL of methanol and placed in a 1 dm tube ?
(1 mark)
- A 6° B -60° C $+60^\circ$ D 0° E cannot determine with data provided

41. If the specific rotation of **i** is -60.0° , what is the specific rotation of **iv**, if 1.0 g of **iv** is dissolved in 10 mL of methanol and placed in a 1 dm tube ?
(1.5 marks)
- A 6° B -60° C $+60^\circ$ D 0° E cannot determine with data provided
42. If the specific rotation of **i** is -60.0° , what is the observed rotation of a sample made up of a mixture of 1 g of **i** and 0.5 g of **v** when dissolved in water (10 mL) and placed in a 10 cm cell ?
(1.5 marks)
- A -9.0° B -60° C $+9.0^\circ$ D 60° E cannot determine with data provided
43. If the specific rotation of **i** is -60.0° , what is the optical purity of a sample of made up of a mixture of 1 g of **i** and 0.5 g of **v** when dissolved in water (10 mL) ?
(1.5 marks)
- A 100% B 66% C 50% D 33% E cannot determine with data provided
44. Assign the absolute configuration to carbon atoms 2 and 4 in compound **ii**.
(1.5 marks)
- A 2R,4R B 2R,4S C 2S,4S D 2S,4R
- E since compound **ii** is meso, the configuration at carbons 2 and 4 cannot be assigned.
45. If the melting point of pure **iv** is 152°C , what is the melting point of pure **v** ?
(1 mark)
- A 152°C B -152°C C lower than 152°C D higher than 152°C
- E cannot determine the melting point of **v** with data provided.

PART 7: SYNTHESIS

10% DESIGN EFFICIENT SYNTHESSES OF ANY THREE (3) of the following target molecules using any of the starting materials shown below.

WRITE YOUR ANSWERS ON THE PAGE PROVIDED.

DO NOT SHOW MECHANISMS.

TARGETS

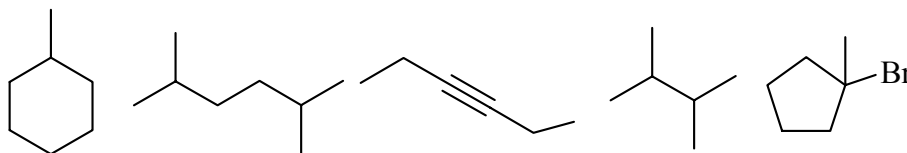
6-oxoheptanoic acid

3-bromo-2,3-dimethylbutane

propanal

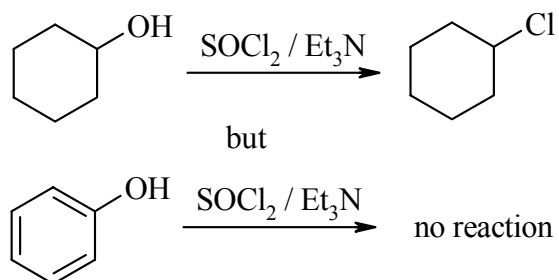
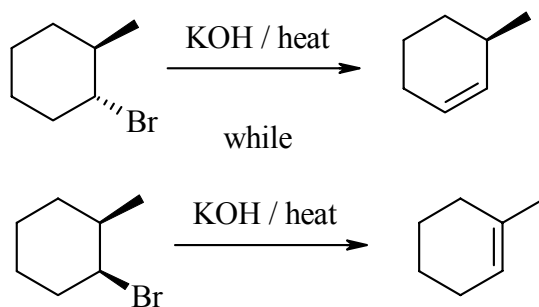
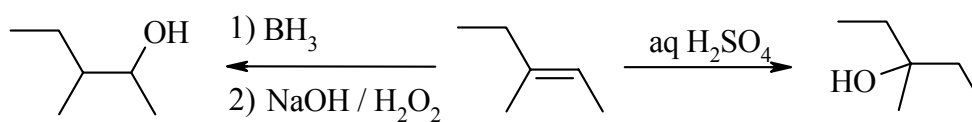
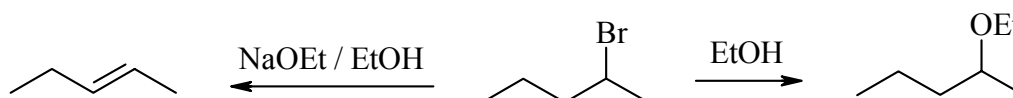
(+/-)-trans-2-methylcyclohexanol

methylcyclopentane

Allowed Starting Materials:

- any organic compounds containing 1 or 2 carbon atoms

In addition you may use any solvents and /or inorganic reagents required

PART 8: MECHANISMS**10% ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.****Using diagrams, mechanisms with curly arrows, and / or short paragraphs, explain the following observations:****I.****II.****III.****IV.**

PART 9: STRUCTURE DETERMINATION**10% WRITE YOUR ANSWER ON PAGE PROVIDED**

The compound **A**, C_8H_{12} , reacted with $Br_2/CHCl_3$ to give a colourless solution. Reaction of **A** with aq. H_2SO_4 gave **B**, $C_8H_{16}O_2$, as a mixture of two stereoisomers, both of which reacted rapidly with the Lucas reagent ($HCl / ZnCl_2$). Subsequent reaction of either of the stereoisomers of **B** by heating with conc. H_2SO_4 gave two isomeric materials, a new compound **C** (major) and the original compound **A** (minor).

Treatment of **C** with aq. H_2SO_4 also gave **B** as the same mixture of two stereoisomers.

Reaction of **A** with ozone followed by a work-up using zinc in acetic acid gave a single product, 3-oxobutanal. In contrast, the similar reaction of **C** with ozone followed by a work-up using zinc in acetic acid, gave a mixture of two products, 2,5-hexanedione and ethanedial.

Reaction of either **A** or **C** with H_2 over palladium gave stereoisomers **E** (major) and **F** (minor), C_8H_{16} .

All the compounds **A - F** are achiral.

Identify the compounds **A - F**.

Explain why the yield of **C** > **A** from the reaction of **B** with conc. H_2SO_4 .

Explain why the yield of **E** > **F** from the reaction of **A** with H_2 / palladium.

****** THE END ******

IRH / BAK